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POTENTIODYNAMIC INVESTIGATION OF THE CORROSION OF IRON

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ABSTRACT

The anodic polarization of iron in sulfuric acid was investigated by the potentiodynamic method. Polarization was performed with an electronic potentiostat which was programmed by a synchronous motor. The effects of potential traverse rate and direction, and electrode pre-treatment are discussed.

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INTRODUCTION

It is now well established that corrosion in aqueous solutions is an electrochemical process influenced by the surface conditions of the corroding metal. Although large amounts of empirical data have been obtained much more work remains to be done to elucidate the mechanisms of corrosion processes. Significant advances in corrosion science may be expected by the application of new instrumental methods to fundamental corrosion studies.

The application of polarization methods for the evaluation of the corrosion behavior of metals and alloys has been widely demonstrated.^{1 - 5} Potentiostatic polarization techniques allow investigation of the corrosion rate of a metal or alloy over a wide range of electrode potentials. For materials which exhibit passivity, the method can be used to study the active-passive transition and the passive state.

The general shape of the anodic polarization curve of a metal or alloy which undergoes the active-passive transition is shown in Figure 1. Commencing from the corrosion potential, as the potential is moved in the noble direction, the current density increases until a maximum is reached. The current and potential at this maximum are called the critical anodic current density, I_c , and the primary passive potential, E_{pp} . When the transition to the passive state occurs, the passive current density, I_p , falls to a low value and remains relatively constant as the potential P is raised. Further increase in potential brings the metal into the transpassive region with an increase in current density and evolution of oxygen. The features of this curve can change significantly with changes in polarization techniques.

There are basically two methods of investigating anodic potentiostatic polarization: steady-state and potentiodynamic. In the steady-state method the potential is maintained at a fixed setting until a steady-state current is obtained. The potential is then moved to another setting and so on until the entire polarization curve is obtained. In practice, the achievement of equilibrium may take hours or perhaps days and therefore very few of the potentiostatic polarization measurements reported in the literature have been conducted under true steady-state conditions. Instead, the potential is usually changed in steps after an arbitrary period of time or after a relatively stable current has been achieved. This variation of the steady-state method is sometimes referred to as the "potential-step" method.

In the potentiodynamic method (also referred to as the potential-sweep or potentiokinetic method) no attempt is made to achieve steady-state conditions. The potentiodynamic method involves continuously changing the potential setting at a constant rate, conveniently done by a small synchronous clock motor, and recording the resultant current. The particular rate which is used is left to the discretion of the investigator. Rates of change of potential have ranged from as high as one volt per minute (1V/min)⁶ to infinitely slow rates.

Although it has been recognized for some time that variations in experimental technique could affect the experimental data, there have been few systematic studies specifically designed to investigate these variables.

Because of this lack of information, it is difficult to generalize on the advantages and disadvantages of the two methods. From the data available in the literature it appears that steady-state determinations offer the advantage of giving more detailed information concerning the shape of the polarization curve. (This assumes that the potential steps are not large.) The disadvantages to this method are that it takes a long time and involves the dissolution of large amounts of material since the specimens remain in the active region for long periods.

If potentiodynamic polarizations are obtained at relatively fast rates, it has the advantage of being able to evaluate the potentiostatic behavior of a series of alloys in a relatively short time. Also, small amounts of the specimens dissolve, and thus the specimen is less disturbed from the conditions which existed at equilibrium corrosion. Furthermore, repeated experiments may be made on the same specimen if this is desired. At the slow potentiodynamic rates one expects to see more details in the polarization curve since equilibrium is approached. Thus, both the steady-state and the potentiodynamic method have advantages and disadvantages. The particular method which an investigator uses should depend upon what he wishes to determine from the data and what metal or alloy is being investigated.

Recent investigations by Littlewood⁷ and Greene⁸ have demonstrated the effect of variation in the rate of potential change on the polarization of stainless steel in sulfuric acid. It was the purpose of this investigation to study the effects of potential rate change and direction and electrode pre-treatment on the potentiostatic polarization of iron in 1N H₂SO₄, studied by the potentiodynamic method. A previous investigation⁹ has studied the steady-state potentiostatic behavior of iron in 1N H₂SO₄.

EXPERIMENTAL

Cylindrical electrodes, with lateral surface areas of approximately 1.25 cm^2 were fabricated from one-half inch Armco iron rod. The analysis of the iron given (in weight percent) by the manufacturer was: C, 0.020; Mn, 0.044; P, 0.003; S, 0.018; Si, 0.004; Cu, 0.092. The electrodes were wet-polished with No. 400 silicon carbide paper, rinsed with demineralized water and stored in a dessicator. For each experiment a new electrode was activated in 5N H_2SO_4 for 30 minutes and then placed in the cell for 16 hours (overnight) before any measurements were taken.

The cell, electrode assembly, and associated electronic equipment have been described previously.⁹ An electronic potentiostat, Wenking Model 61-TR, modified with a small synchronous motor was used to generate the potential sweeps. Two rates were used: 0.36 V/hr. and 12 V/hr., referred to in this report as the slow and fast rates, respectively. Current and potential were recorded simultaneously as a function of time on a Leeds & Northrup Company two-pen recorder.

The 1N H_2SO_4 solutions were prepared from Analytical Reagent grade H_2SO_4 and de-ionized water. The solutions were deaerated for at least 16 hours with nitrogen before inserting the electrode assembly; the nitrogen flow was continued throughout the experiments. Temperatures of the solutions were $25 \pm 1^\circ \text{C}$.

RESULTS AND DISCUSSION

Three experimental variables in the potentiostatic anodic polarization were studied in this investigation, using the potentiodynamic technique. First, the effect of variation in the anodic polarization rate was investigated. This was accomplished by conducting experiments at a fast rate, 12 V/hr., and a slow rate, 0.36 V/hr. The second effect studied was the direction of polarization. This was done by first polarizing in the noble direction beginning at the corrosion potential and ending at +2.0 V, relative to a saturated calomel electrode (s.c.e.); then the same electrode was polarized back down in the active direction to the corrosion potential. The third effect studied was the electrode pre-treatment, or history. This was done by re-polarizing used electrodes and comparing the results to data obtained on newly-polished and activated electrodes.

Typical polarization curves are given in Figures 2 to 4. Selected times on the continuously recorded charts were used to obtain the data for each point plotted in these figures. Figure 2 illustrates an anodic polarization of a new electrode at the fast rate. First the electrode was polarized in the noble direction, starting from the corrosion potential

-0.480 V vs. s.c.e.; then it was held at +2.0 V for ten minutes and finally polarized in the active direction. Figure 3 shows an anodic polarization at the fast rate of a used electrode. This electrode was actually the same as that described by Figure 2, re-polarized four hours later from a corrosion potential of -0.483 V.

Figure 4 illustrates the anodic polarization of a new electrode at the slow rate. This polarization was done in the noble direction, starting from the corrosion potential of -0.480 V. The data from these experiments is listed in Table I.

At the fast polarization rate, the iron showed higher current densities at equivalent potentials than was the case for the slow rate. This was especially evident at the primary passive potential and in the passive region. After the primary passive potential, an unstable region of about 200 mV was observed at the fast rate during the active-passive transition. During this period, the current density underwent large, rapid fluctuations.

At the slow polarization rate, the stable active region extended to more noble potentials and the transition from active to passive was more abrupt showing only a small region of about 30 mV where the current density was unstable. The effects of polarization rate and direction and electrode pre-treatment on the primary passive potential, critical anodic current density, and minimum passive current density are summarized in Table II.

An important effect is seen to be the change in the critical anodic current density. At the fast rate of potential change the critical anodic current density was higher than at the slow rate. This implies that the process of passivation actually begins in the active region and becomes the controlling step at the primary passive potential. Since the electrode remains in the active region for longer periods of time at the slow rate this allows the barrier-film to form and passivation to occur at lower current densities. These effects are in agreement with the hypothesis suggested by Kolotyrkin.¹⁰ It was also observed that the minimum passive current density was at least an order of magnitude lower at the slow polarization rate.

The more common method of anodic polarization begins at the corrosion potential and the polarization is done in the noble direction, i.e., the potential is increased. The lowest passive current density (at the fast rate) was obtained when the procedure followed was to start at +2.0 V vs. s.c.e. in the transpassive region and then to polarize down to the corrosion potential. This feature could be of importance in systems which are anodically protected and warrants further investigation.

Recycling of a specimen, that is, subjecting the same specimen to additional polarization, is illustrated in Figure 3. It caused the primary passive potential to be raised and the unstable voltage range between the primary passive potential and a stable passive potential to be much decreased as was the case with the slow polarization of a new specimen. It was found that new specimens polarized in H_2SO_4 solutions contaminated by corrosion products from previous experiments showed essentially the same polarization characteristics as new electrodes in new solutions, indicating that solution effects were not as important as the previous history of the specimen, i.e., using a new electrode or an electrode which had previously been polarized.

The results show the dependence of polarization behavior on (1) the rate and direction of polarization, and (2) the previous history of specimens. At the slowest rates, the conditions which exist during steady-state polarization are approached. At the higher rates, greater current densities are required for passivation to occur, but the total number of coulombs passed is smaller and thus the surface is less disturbed from the condition which existed at the corrosion potential. When attempting to compare the results of different investigations, it is clear that in order to attach any significance to such parameters as E_{pp} , I_c , I_p , it is necessary to define the experimental method completely, especially including the rate of potential change. Because of the variations in technique of the investigators, it is difficult to compare published anodic polarization curves of an active-passive system.

The variations due to specimen history have been explored briefly and further investigation appears necessary to clarify what causes these variations. Also the method of polishing specimens could be important. For the purpose of comparing the polarization characteristics of different alloy specimens, it would be advisable to use identical surface preparation techniques and only to use new electrodes for each experiment.

The optimum rate at which a specimen should be polarized will depend on the purpose of the experiment. If the purpose is to investigate the detailed structure of the polarization curve, then the slowest possible rate should be used since faster rates tend to obscure the passive region and other features of the polarization curve. However, if the purpose is to evaluate the corrosion resistance of a series of alloys, then the faster rate would be desirable, since the electrode is less disturbed from conditions which existed at the corrosion potential.

FUTURE WORK

Corrosion is an important factor which should be considered in the design of any structure. This is especially important for structures located in a marine environment since the corrosive effects of sea water on metals are considerable. The synthesis of corrosion-resistant structural materials and the development of new methods for controlling corrosion will greatly aid the civil engineer in solving difficult design problems.

This report is the second in a series which will deal with the investigations of the electrochemical characteristics of various electrode-electrolyte systems. The long range objective of these investigations is the elucidation of the mechanisms of the electrochemical and physical transformations that occur at electrode-electrolyte interfaces. Intimate knowledge of the details of these transformations is of vital importance in the prevention and control of corrosion.

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Table I. Potentiodynamic Polarization of Iron in 1N Sulfuric Acid

Potential vs. s.c.e. (mV)	Current Density (ma/cm ²)				Polarization Rate, 0.36 V/hr., New Electrode Noble Direc- tion
	Polarization Rate 12 V/hr.				
	New Electrode		Used Electrode		
	Noble dir.	Active dir.	Noble dir.	Active dir.	
-450					0.10
-440	0.47	3.2	0.19	4.2	
-400	2.3	9.1	1.1	9.1	2.2
-300	38.	42.	18.	43.	6.8
-200	17.	80.	36.	91.	12.
-100	27.	125.	31.	136.	19.
0	58.	167.	46.	185.	29.
+100	125.	212.	55.	231.	38.
+200	228.	261.	70.	280.	50.
+300	402.	302.	91.	322.	59.
+400	398.	*	121.	379.	68.
+500	*	0.38	114.	530.	79.
+600	*	0.43	121.	0.76	105.
+700	8.3	0.54	129.	0.49	0.020
+800	7.6	0.61	136.	0.49	0.020
+900	3.6	0.66	170.	0.55	0.020
+1000	2.5	0.99	234.	0.62	0.020
+1100	2.0	1.5	295.	0.69	0.026
+1200	0.83	2.0	387.	0.83	0.054
+1300	0.91	2.6	23.	1.1	0.21
+1400	1.1	3.6	6.8	1.4	0.29
+1500	1.2	4.7	5.3	1.4	0.46
+1600	1.2	3.4	3.6	2.4	6.7
+1700	9.1	12.	11.	9.9	11.4
+1800	41.	38.	39.	32.	19.4
+1900	76.	67.	68.	57.	
+2000	106.	106.	91.	91.	

* Unsteady

Table II. Anodic Potentiostatic Polarization Characteristics of Armco Iron in 1N Sulfuric Acid, Studied by the Potentiodynamic Method

Polarization Rate (V/hr.)	Polarization Direction and Starting Potential	Primary Passive Potential, E_{pp} , vs. s.c.e.	Critical Anodic Current Density (ma/cm ²)	Minimum Passive Current Density (ma/cm ²)
12	Noble, start at corr. pot. (new electrode)	+300	402	0.83 (+1.2 V)
12	Active, start at 2.0 V (s.c.e.) (new electrode)	+360	310	0.38 (+0.5 V)
0.36	Noble, start at corr. pot. (new electrode)	+670	190	0.02 (+1.0 V)
12	Noble, start at corr. pot. (used electrode)	+1200	387	3.6 (+1.6 V)
12	Active, start at 2.0 V (s.c.e.) (used electrode)	+500	530	0.49 (+0.7 V)

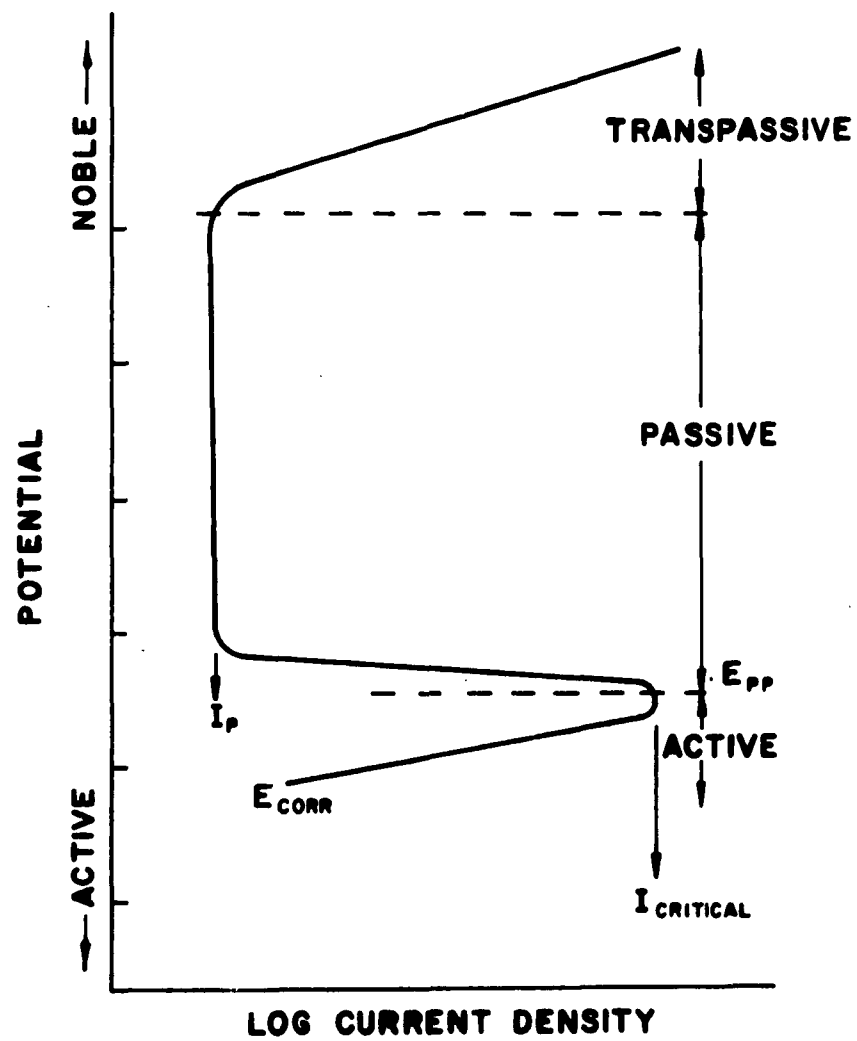


FIG.1

**POTENTIOSTATIC
ANODIC POLARIZATION
(SCHEMATIC)**

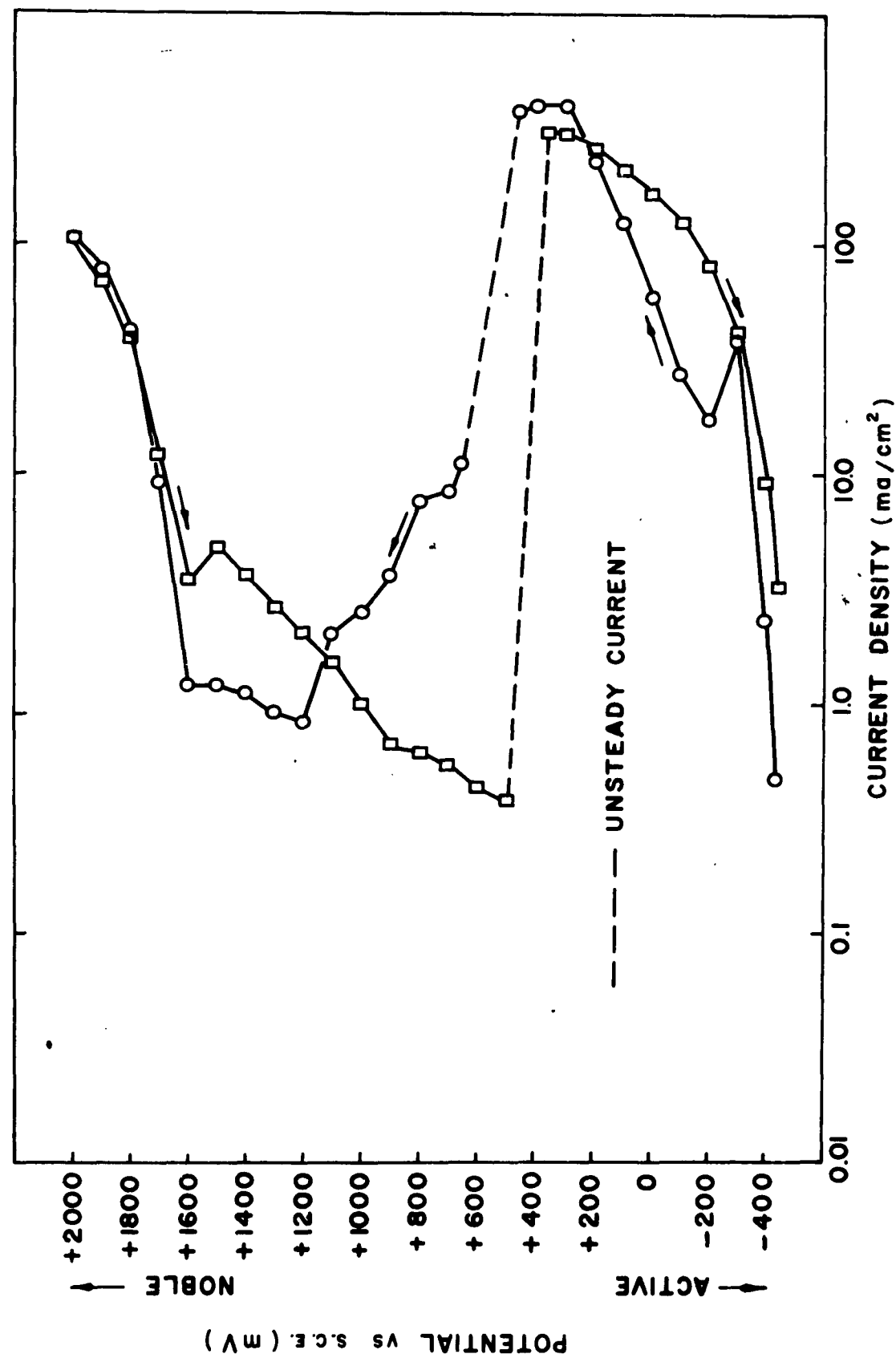


FIG. 2 ANODIC POLARIZATION OF ARMCO IRON (NEW ELECTRODE)
IN 1N H₂ SO₄ AT A RATE OF 12 V/HR.

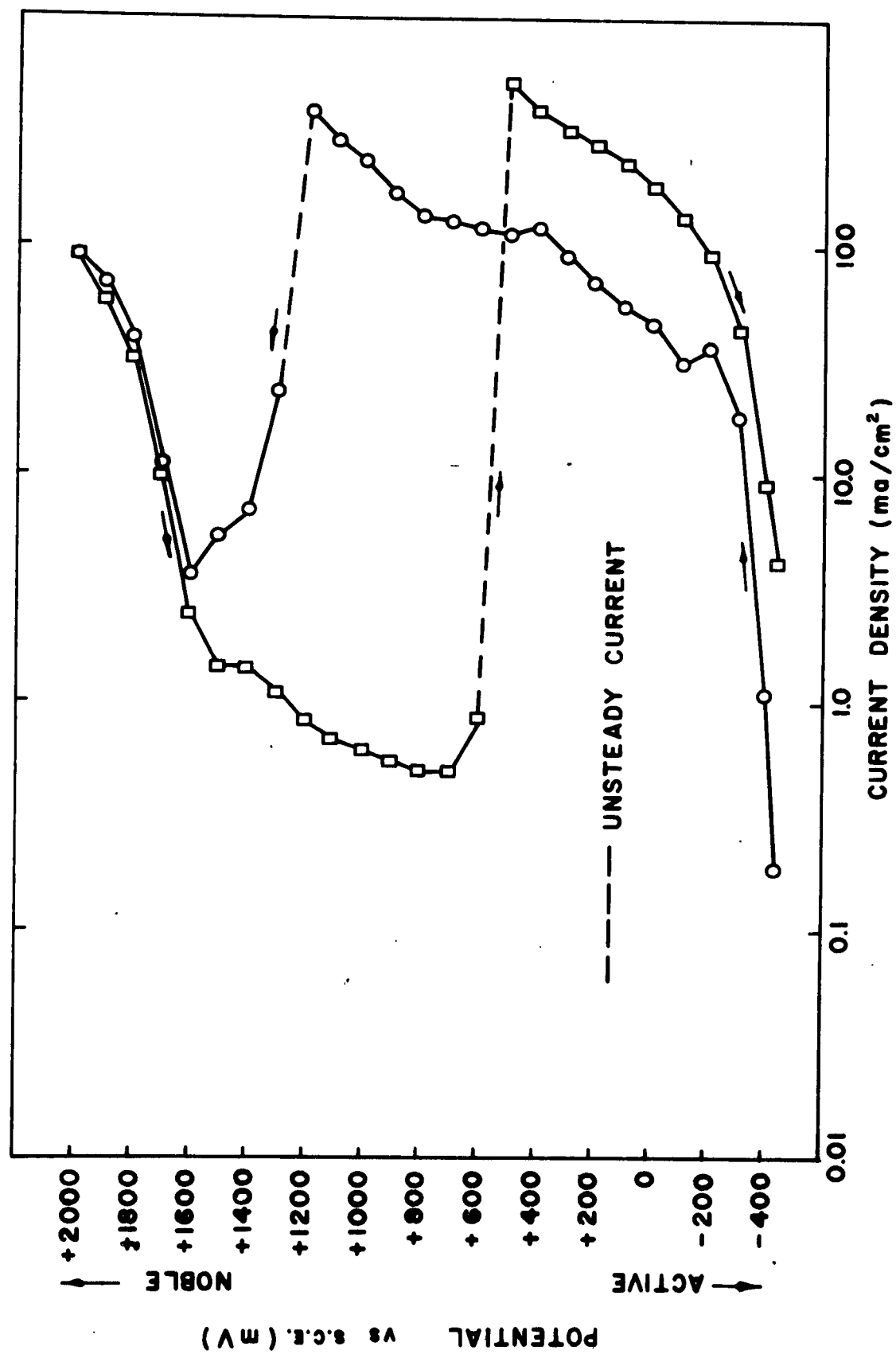


FIG. 3 ANODIC POLARIZATION OF ARMCO IRON (USED ELECTRODE) IN 1 N H₂ SO₄ AT A RATE OF 12 V/HR.

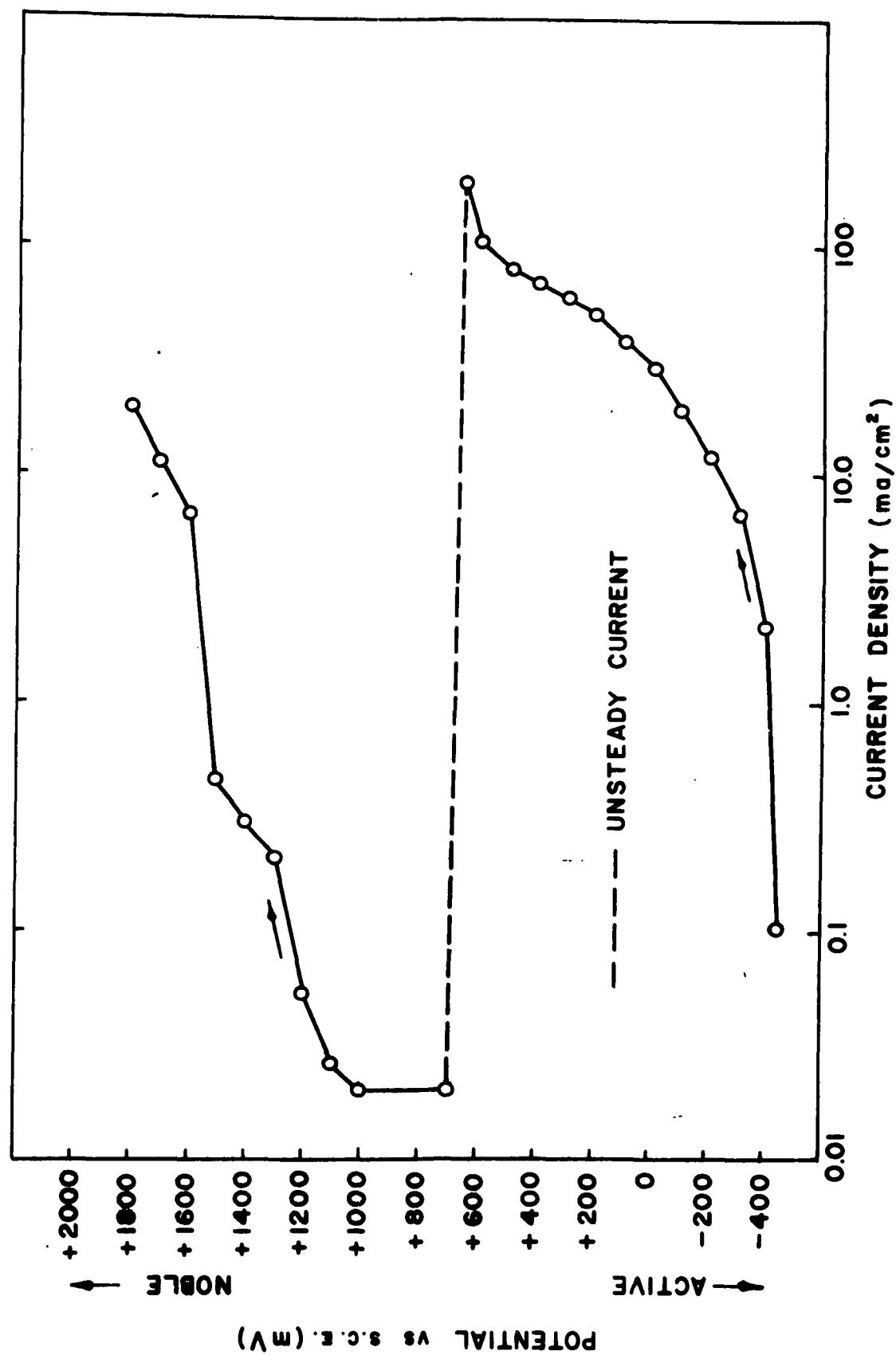


FIG. 4 ANODIC POLARIZATION OF ARMCO IRON (NEW ELECTRODE)
IN IN H₂ SO₄ AT A RATE OF 0.36 V/HR.